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Chiral diketopyrrolopyrrole-helicene polymer with efficient red circularly polarized luminescence

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Keywords: helicene, diketopyrrolopyrrole, circularly polarized luminescence, red emitters, exciton coupling, chiral polymers

Abstract

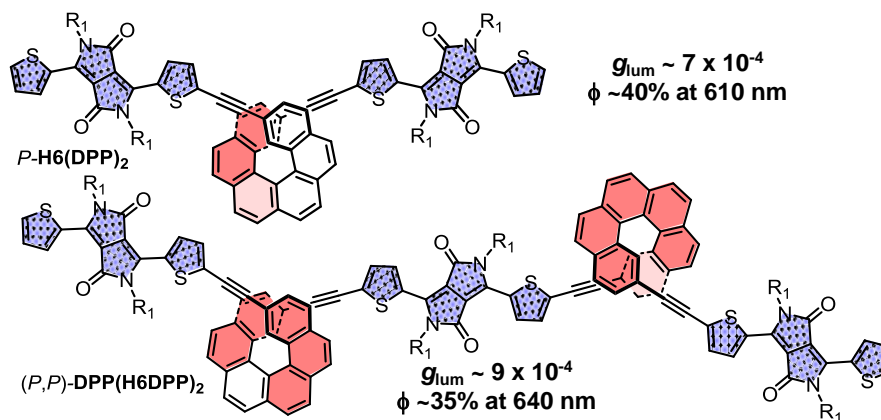
Chiral diketopyrrolopyrrole (DPP)-helicene polymers were synthesized to develop efficient red circularly polarized (CP) light emitters. These original chiral dyes display intense electronic circular dichroism (ECD) and CP luminescence (CPL) in the far-red spectral region owing to the presence of excitonic coupling between achiral DPP within the chiral environment of the polymeric structure. This work affords an interesting example illustrating the potential of π -conjugated helical polymers for chiral optoelectronic applications.

1 Introduction

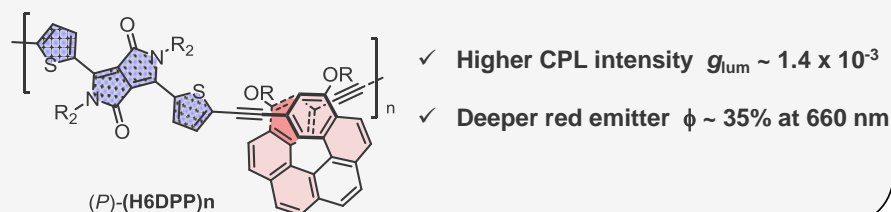
Circularly polarized (CP) light has received renewed attention owing to its superior potential over unpolarized one in a diverse range of domains such as (chir)optoelectronics (stereoscopic displays, organic light-emitting diodes (OLEDs), optical information processing, etc.) as well as in bio-imaging and chiral sensing (Berova et al., 2000; Berova et al., 2012; Riehl and Richardson, 1986; Maeda and Bando, 2013; Kumar et al., 2015; Hiroki et al., 2018; Longhi et al., 2016; Francesco and Lorenzo, 2015; de Bettencourt-Dias, 2014; Carr et al., 2012; Zinna et al., 2015; Brandt et al., 2016, Zinna et al., 2017; Zinna and Di Bari 2018; Han et al., 2018; Meng et al., 2017). Until recently, luminescent chiral lanthanides complexes have been the most studied molecular CPL emitters since this family of compounds can display relatively high level of circularly polarized emission,

36 characterized by a luminescence dissymmetry factor $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, of more than 1 (Carr et
 37 al., 2012; Zinna et al., 2015; Zinna and Di Bari, 2018). However, lanthanide complexes often possess
 38 low luminescent quantum yield (ϕ) and stability issues, which may difficultly render their integration
 39 in optoelectronic devices such as CP-OLEDs, chiral photovoltaics and transistors for example. To
 40 circumvent these aspects, the development of chiral emitting small organic molecules (SOM) has
 41 gained increasing interest, also benefiting from their tunable photophysical and chiroptical properties
 42 from the blue to the near-infrared spectral region (Carr et al., 2012; Zinna et al., 2015; Zinna and Di
 43 Bari, 2018). One particularly appealing synthetic strategy to design efficient CPL emitters has
 44 consisted in developing chirally perturbed π -extended achiral chromophores, mostly based on C_2 -
 45 symmetric chiral moieties (chiral binaphthyl or 1,2-diamino-cyclohexane derivatives) linked to
 46 bodipy or perylene organic dyes (Kumar et al., 2013; Kumar et al., 2014; Sheng et al., 2016;
 47 Tsumatori et al., 2010; Kumar et al., 2015; Langhals et al., 2011; Sánchez-Carnerero et al., 2014). In
 48 addition, helicenes have recently shown to be very good scaffolds for the development of emissive
 49 materials with strong CPL activity (Chen and Shen, 2016; Gingras, 2013; Dhbaibi et al., 2018;
 50 Dhbaibi et al., 2020; Zhao et al., 2019; Shen et al. 2020). Following this approach, we recently
 51 reported helical π -conjugated helicene-diketopyrrolopyrrole (DPP) dyes (*P*-**H6(DPP)**₂ and (*P,P*-
 52 **DPP(H6DPP)**₂, Figure 1) (Dhbaibi et al., 2018) as red CPL emitters, (Nishimura et al., 2017; Sakai
 53 et al., 2016, Pascal et al., 2016; Shen et al., 2014; Saleh et al., 2015; Biet et al., 2017) arising from an
 54 intramolecular exciton coupling (Harada et al., 2012) between the achiral DPP units placed within the
 55 chiral environment of the helicene. Based on purely π - π^* transitions, this design afforded promising
 56 g_{lum} factors of $6-9 \times 10^{-4}$ at 610-650 nm associated with fluorescence quantum yields (ϕ) of 35-40 %.
 57 To our knowledge, this study remains the only example of DPP based CPL emitters, despite the
 58 promising potential of diketopyrrolopyrrole and its derivatives in a broad range of applications such
 59 as OLEDs, photovoltaic devices, organic transistors, and fluorescent probes (Data et al., 2016; Kaur
 60 and Choi, 2015; Heyer et al., 2015; Nielsen et al., 2013; Grzybowski and Gryko, 2015).

Previous work: Chiral exciton coupling of achiral DPP (Dhbaibi et al., 2018)



This work: Helical polymer DPP based CPL emitters



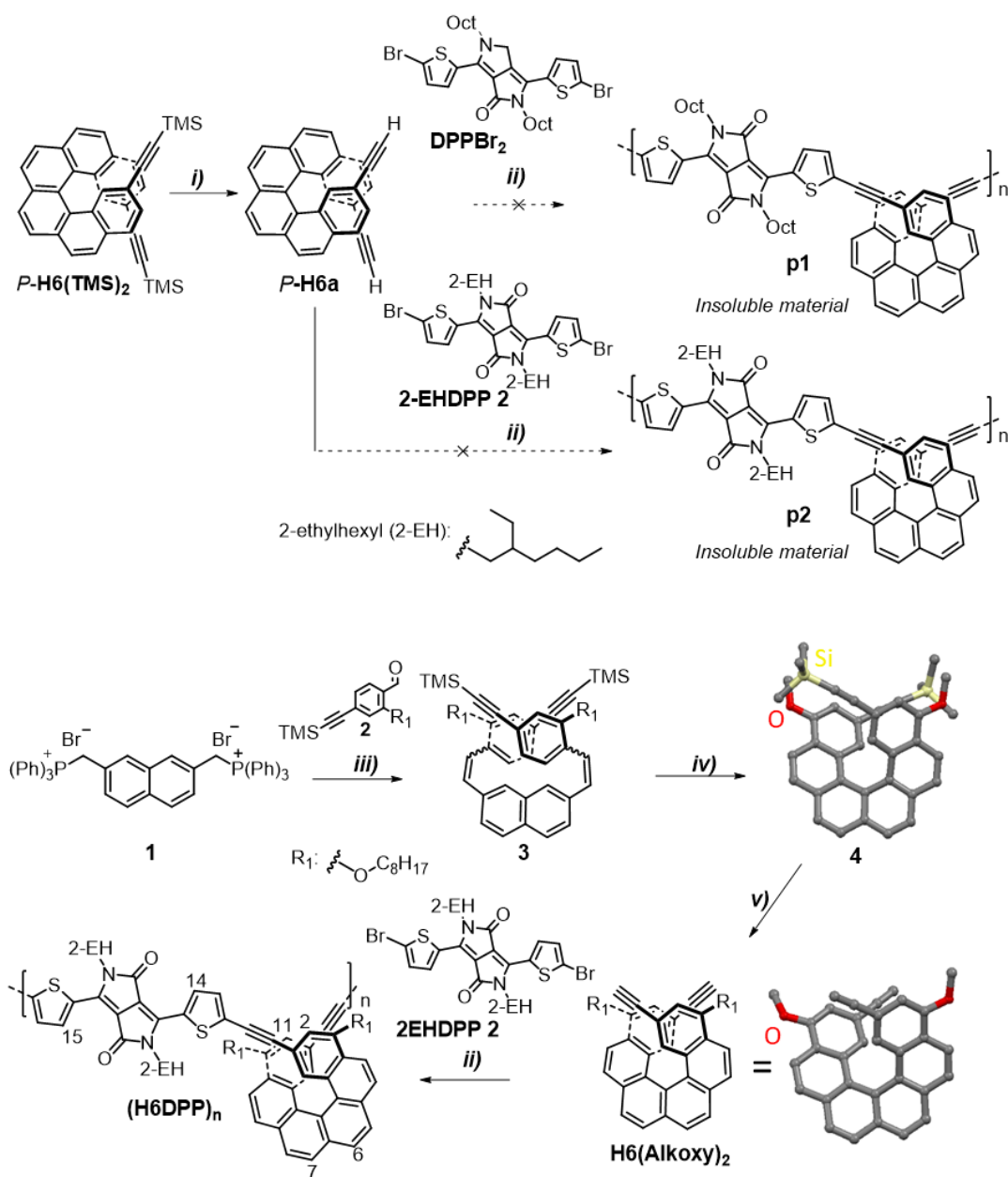
62 **FIGURE 1.** Chemical structures of CPL emitters based on helicene-diketopyrrolopyrrole polymers
63 and their corresponding polarized and unpolarized luminescence characteristics (*P* enantiomers are
64 shown).

65 With the aim of deeper exploring this innovative and promising synergy between chiral helicene and
66 achiral diketopyrrolopyrrole dye, we report here the synthesis and chiroptical properties of novel π -
67 conjugated helical polymeric CPL emitters, namely *rac*-, (*P*)- and (*M*)-(**H6DPP**)_n, Figure 1. These
68 new examples of helicene-diketopyrrolopyrrole association displays intense electronic circular
69 dichroism (ECD) in the visible region and strong red CPL with $g_{\text{lum}} = 1.4 \times 10^{-3}$ at 660 nm,
70 associated with a high ϕ of ~35 %. This first example of chiral helicene-DPP based polymer exhibits
71 higher CPL response than the molecular chiral helicene-DPP dyes previously reported, and brings
72 interesting aspects for the design of efficient polymeric red and near infra-red CPL emitters.

73 **Results and discussion**

74 **Synthesis of polymer (**H6DPP**)_n**

75 The helicene-DPP polymers were prepared using the Sonogashira coupling between a helicene
76 decorated with two alkynyl functions and a DPP core substituted with two bromothiophene units. In a
77 first attempt to synthesize polymer (**H6DPP**)_n, the coupling was performed using enantiopure *P*- and
78 *M*-2,15-bis-(ethynyl)[6]helicene (*P*- and *M*-**H6a**) (Anger et al., 2012) with 3,6-bis(5-bromothiophen-
79 2-yl)-2,5-diketopyrrolopyrrole, **DPPBr**₂, respectively (Figure 2, where only *P* enantiomer is
80 described) (Wu et al., 2015). While the reactions seemed to proceed efficiently, they resulted in the
81 formation of insoluble dark blue material (**p1**, Figure 2). To circumvent this solubility issue, we
82 introduced widely used branched 2-ethylhexyl (2-EH) chains on the DPP unit in place of the linear
83 octyl ones (Palai et al., 2010; Huo et al., 2009). Although this fragment has a chiral center, we used
84 its racemic form since a weak influence of these additional stereogenic centers is expected on the
85 photophysical and chiroptical properties of the final polymer in diluted solution. Unfortunately, this
86 new approach also afforded insoluble blue solid when a stoichiometric mixture of *P*-**H6a** and
87 **2EHDPP 2** was subjected to the Sonogashira coupling conditions (**p2**, Figure 2). To further increase
88 the solubility of the obtained polymer material, the helicenic fragment was also functionalized with
89 additional linear octyloxy chains through a new synthetic pathway involving 2-(octyloxy)-4-
90 ((trimethylsilyl)ethynyl)benzaldehyde, **2**, as starting material for the synthesis of the helicene
91 fragment. Indeed, the latter was engaged in a double Wittig reaction with naphthyl-2,7-
92 dimethylphosphonium bromide salt, **1**, to give 2,7-bis(2-(octyloxy)-4-
93 ((trimethylsilyl)ethynyl)styryl)naphthalene, **3**, in 60% yield. The resulting *cis/trans* stilbene mixture
94 was subsequently submitted to a photocyclisation reaction with propylene oxide as an acid scavenger
95 to afford *rac*-2,15-bis-((trimethylsilyl)ethynyl)-4,13-bis-(octyloxy)[6]helicene (**4**) in 50% yield,
96 followed by deprotection reaction of the two remaining TMS groups to yield **H6(Alkoxy)**₂ (Scheme
97 1). Fully characterized by NMR spectroscopy and mass spectrometry (see ESI), the structures of the
98 two latter were further ascertained by X-ray crystallographic analysis (see Scheme 1 and ESI). Both
99 *rac*-**4** and *rac*- **H6(Alkoxy)**₂ crystallized in a *P*-1 space group and displayed helicity (dihedral angle
100 between the two terminal rings) of 41.1° and 54.4°, respectively, which is in the range of classical
101 carbo[6]helicenes (Chen and Shen, 2016; Gingras, 2013; Dhbaibi et al., 2019). Moreover, the lateral
102 octyloxy chains point toward the outside of the molecules, which may disfavor the formation of
103 polymer aggregates in solution.



104

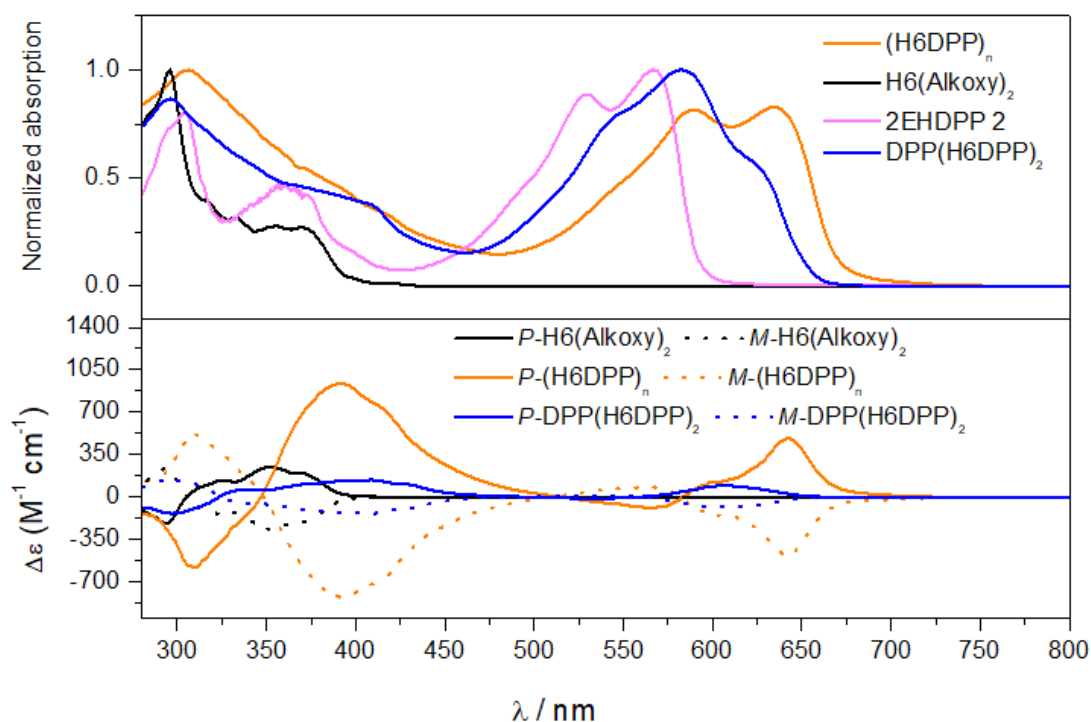
105 **FIGURE 2.** Synthesis of enantiopure P -(**H6DPP**)_n. TMS: trimethylsilyl. Reaction conditions: *i*)
 106 TBAF, CHCl₃; *ii*) Pd(PPh₃)₄, CuI, Et₃N/toluene, 50 °C; *iii*) *n*-BuLi, THF, -78 °C to rt, 60%; *iv*) hv, I₂
 107 (1 equiv.), propylene oxide (50 equiv.), toluene, 50%; *v*) TBAF, CHCl₃, 52%, chiral HPLC. X-ray
 108 crystal structures of *rac*-**4** and *rac*-**H6(Alkoxy)**₂ (octyl chains and hydrogen atoms have been omitted
 109 for clarity).

110 *Rac*-**H6(Alkoxy)**₂ was then submitted to chiral HPLC separation to give P -(+) and M -(-) in 99% and
 111 98.5% of *ee*, respectively (see ESI for detailed experimental conditions). These enantiomers, as well
 112 as the racemic compound, were finally engaged in the polymerization reaction with **2EHDPP 2** and
 113 gave expected soluble polymers which were firstly filtered over a silica plug, then further purified by
 114 size-exclusion chromatography (SEC, CHCl₃) before precipitated using CHCl₃/MeOH solvent
 115 mixture to yield P -, M - and *rac*-(**H6DPP**)_n in approximately 45% yield for each polymer (see ESI).
 116 These novel chiral dyes are soluble in common organic solvents such as THF, CHCl₃, and CH₂Cl₂,
 117 and were characterized by ¹H NMR and SEC using a polystyrene standard in THF. The obtained

118 NMR spectrum displays characteristic signals for both helicene and DPP starting materials: for
119 instance, shielded H^{2,11} and deshielded H^{6,7} helicenic protons at 6.75 and 8.50 ppm respectively, and
120 deshielded DPP protons H^{14,15} at 9.10 ppm (see ESI). The number average molecular mass (M_n) for
121 *rac*-, *P*-, and *M*-(**H6DPP**)_n were estimated to be 6.9×10^3 , 5.3×10^3 and 6.4×10^3 , respectively,
122 which correspond to a low degree of polymerization, *ca.* 5-6 (helicene-DPP) units (See ESI). The
123 thermal stability of *rac*-(**H6DPP**)_n was also evaluated by thermogravimetric analysis (TGA) and
124 resulted in an onset decomposition temperature at 300 °C with a 10% weight loss.

125 **UV-Vis, ECD and electrochemical characterizations**

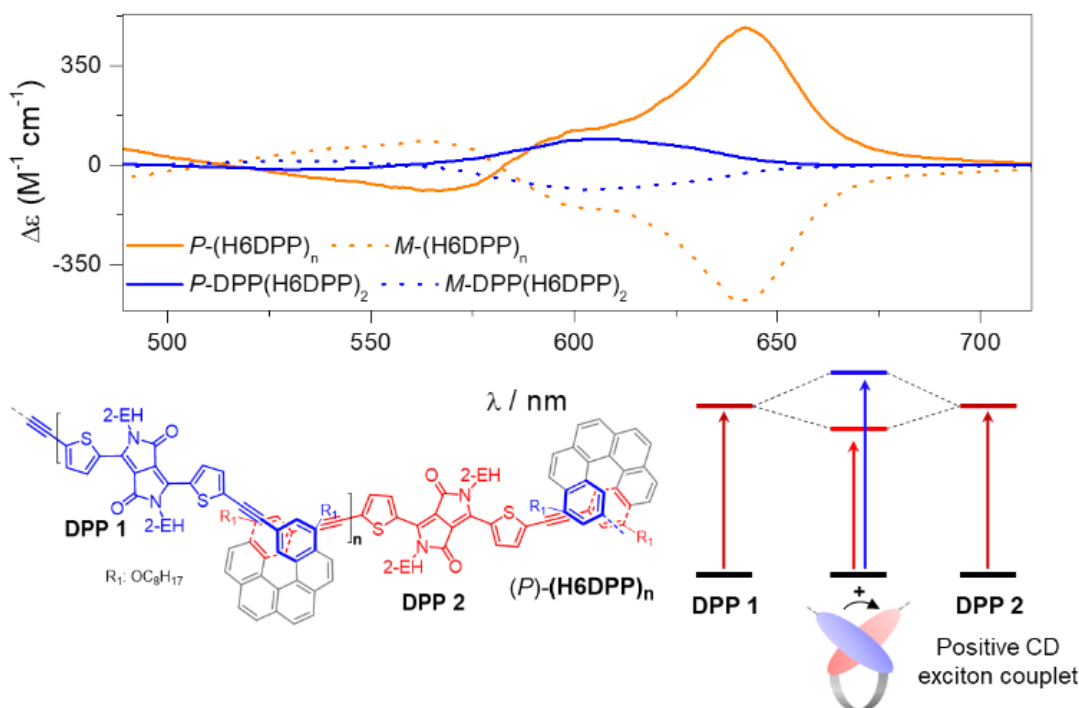
126 The ground state photophysical and chiroptical properties of DPP-helicene polymers were
127 investigated in CH₂Cl₂ solutions and compared with corresponding precursors and previously
128 reported **DPP(H6DPP)**₂. UV-Vis spectrum of (**H6DPP**)_n polymer displays two main absorption
129 signatures between 300 and 425 nm and between 530 and 675 nm that correspond to a combination
130 of helicene and DPP transitions for the higher energy region and only from DPP transitions for the
131 low energy part. The latter absorption region is red-shifted by 70 nm in comparison with DPP
132 precursor, characterized by $\epsilon = 7.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 565 nm and $35 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 635 nm for
133 **2EHDPP 2** and (**H6DPP**)_n, respectively, resulting from the extension of the π -conjugation via the
134 alkynyl bridges between the DPP dye and the helicene units. These observations are supported by
135 comparison with **DPP(H6DPP)**₂ UV-vis spectrum, where contributions of both “DPP-helicene” and
136 “helicene-DPP-helicene” fragments are superposed in the red region (see ESI for additional details).
137 Going from oligomer **DPP(H6DPP)**₂ to polymer (**H6DPP**)_n does not strongly red-shift the overall
138 absorption signature ($\lambda_{\text{max}} = 620$ and 635 nm for **DPP(H6DPP)**₂ and (**H6DPP**)_n lowest absorption
139 bands, respectively), which suggests that electronic communication between each bis(ethynyl)DPP
140 unit through the π -conjugated helicene is relatively limited along the polymer. The observed
141 difference of 15 nm results probably from the presence of the electron donating octyloxy groups on
142 the helicene fragment for (**H6DPP**)_n.



143

144 **FIGURE 3.** UV-vis (top) and ECD (bottom) spectra of **H6(Alkoxy)₂** (black), **2EHDPP 2** (purple),
 145 **DPP(H6DPP)₂** (blue) and **(H6DPP)_n** (orange) in CH₂Cl₂ at 298 K (~10⁻⁵ M).

146 ECD of *P*- and *M*-**(H6DPP)_n** displays expected mirror-image spectra with intense responses ranging
 147 from 280 to 700 nm (Figure 3). *P*-**(H6DPP)_n** exhibits an intense negative ECD band ($\Delta\epsilon = - 576 \text{ M}^{-1} \text{ cm}^{-1}$)
 148 at 309 nm which is 19 nm red-shifted compared to helicene *P*-**H6(Alkoxy)₂**, a broad strong
 149 positive band between 347 and 500 nm with a maximum at 391 nm ($\Delta\epsilon = + 940 \text{ M}^{-1} \text{ cm}^{-1}$) and a
 150 shoulder at 414 nm ($\Delta\epsilon = + 740 \text{ M}^{-1} \text{ cm}^{-1}$), a negative contribution at 565 nm ($\Delta\epsilon = - 88 \text{ M}^{-1} \text{ cm}^{-1}$)
 151 followed by a positive one with a maximum at 640 nm ($\Delta\epsilon = + 481 \text{ M}^{-1} \text{ cm}^{-1}$). This lowest bisignate
 152 DPP-centered signal is clearly reminiscent of what we observed for *P,P*-**DPP(H6DPP)₂** (Figure 4),
 153 which was attributed to a chiral excitonic coupling between the DPP-centered π -orbitals in the helical
 154 arrangement (Dhbaibi et al., 2018; Bouvier et al., 2018; Dhbaibi et al., 2020). Elongating the number
 155 of helicene-DPP association within polymer *P*-**(H6DPP)_n** appears as an efficient strategy to obtain
 156 very intense ECD signature across the whole spectrum and especially in the red region thanks to the
 157 increase of the excitonic coupling intensity. Indeed, this higher sensitivity to red circularly polarized
 158 light for *P*-**(H6DPP)_n** is confirmed by the evaluation of the associated dissymmetry factor $g_{\text{abs}} = \Delta\epsilon/\epsilon$
 159 $= +1.8 \times 10^{-3}$ at 649 nm, i.e. a 40 % increase in comparison with *P,P*-**DPP(H6DPP)₂** ($g_{\text{abs}} = +1.3 \times$
 160 10^{-3} at 610 nm).



161 **FIGURE 4.** Enlargement of 490-710 nm region of the ECD spectra of **DPP(H6DPP)₂** (blue) and
 162 **(H6DPP)_n** (orange) in CH₂Cl₂ at 298 K (~10⁻⁵ M), with schematic illustration of the chiral exciton
 163 coupling process in **(H6DPP)_n**.

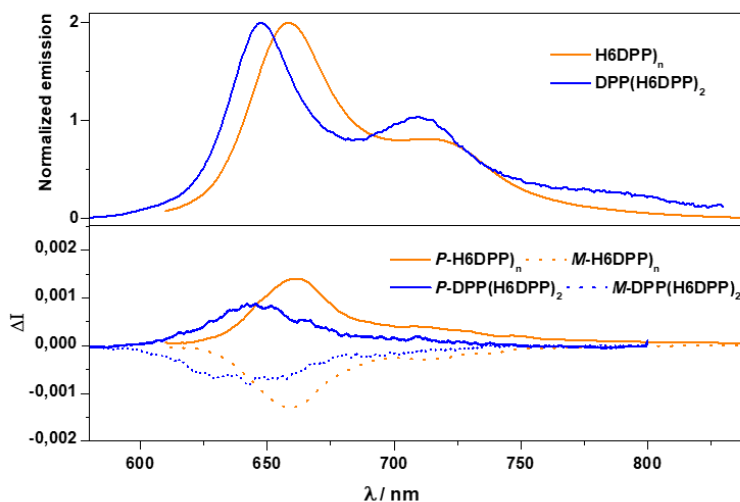
164 The electrochemical behavior of **(H6DPP)_n** was investigated by cyclic voltammetry (CV, Figure
 165 S17, Table S1), which displays pseudo-reversible oxidation process at ca. +0.81 V and a reversible
 166 reduction one at -1.24 V vs. SCE, respectively assigned to the oxidation and the reduction of the DPP
 167 unit(s). The calculated HOMO and LUMO energy level were -5.21 eV and a LUMO level of -3.16
 168 eV, respectively, leading to an estimated electrochemical band gap of 2.05 eV.

169 **Unpolarized (PL) and circularly polarized luminescence (CPL)**

170 To our delight, **(H6DPP)_n** displays intense unpolarized vibronic emission arising from the DPP-
 171 ethynyl fragment with a maximum intensity at 660 nm and a quantum yield of 35 %. Interestingly,
 172 these values suggest that embedding DPP-helicene fragment within a polymer material is also an
 173 efficient strategy to make deeper red emitter while keeping a high fluorescence efficiency since
 174 **DPP(H6DPP)₂** exhibits similar luminescence quantum yield ($\phi = 35\%$) but its emission is blue
 175 shifted ($\lambda_{\text{max}} = 650$ nm). In order to rule out the possibility of charge transfer character the emission
 176 of the polymer was carried out in solvents of different polarity including toluene, tetrahydrofuran and
 177 dichloromethane in which the polymer was fully soluble (Figure S13). A similar spectral behavior
 178 was found in these solvents with a structured signals and no significant shift of the emission spectra,
 179 indicating that the nature of the emission is mainly based on π - π^* transitions localized on the DPP
 180 units. The fluorescence kinetics of the polymer was also performed at 650 nm (Figure S14) and
 181 nicely fits a single-exponential decay function with a decay time constant of 2.08 ns.

182 Regarding circularly polarized luminescence (CPL), mirror-image spectra were also obtained for *P*-
 183 and *M*-**(H6DPP)_n** with a maximum and a structural signature similar to unpolarized emission,
 184 highlighting the synergy of the DPP-helicene association also in the polymer chiral excited-state
 185 (Figure 5). Moreover, g_{lum} factor of $+1.3 \times 10^{-3}$ was determined for *P*-**(H6DPP)_n**, which suggests a

186 relatively similar chiral geometry of the ground and emitting excited states ($g_{\text{lum}}/g_{\text{abs}} = 0.72$) and
 187 represents also a *ca.* 40 % increase in comparison with *P,P*-DPP(H6DPP)₂ ($g_{\text{lum}} = +0.9 \times 10^{-4}$). The
 188 obtained g_{lum} values for polymers (H6DPP)_n are in the same range of reported SOM CPL emitters
 189 ($10^{-4} - 10^{-2}$), and are among the most efficient ones for the far red and near infrared region (*i.e.* for
 190 $\lambda_{\text{max}} > 650 \text{ nm}$, $3 \times 10^{-4} < g_{\text{lum}} < 4.3 \times 10^{-3}$) (Hiroki et al., 2018).



191

192 **FIGURE 5.** Normalized fluorescence (top) and CPL (bottom) spectra of DPP(H6DPP)₂ (blue) and
 193 (H6DPP)_n (orange) in CH₂Cl₂ at 298 K. CPL spectra for *P* and *M* enantiomers are shown
 194 respectively in solid and dotted lines.

195 Conclusions

196 In summary, we have successfully prepared novel helical conjugated polymers based on the
 197 association between enantiopure carbo[6]helicene derivative and diketopyrrolopyrrole dye via the
 198 Sonogashira cross-coupling. These polymers show strong ECD signal in the visible region ($\Delta\epsilon = 482$
 199 $\text{M}^{-1} \text{cm}^{-1}$ at 642 nm, for *P*-(H6DPP)_n) and strong CPL emission response signals ($g_{\text{lum}} = +1.3 \times 10^{-3}$
 200 at 662 nm) along with high fluorescence quantum efficiency ($\phi_f = 35 \%$). Extending the efficiency of
 201 exciton coupling process in chiral polymers allow efficient preparation of CPL emitters deeper in the
 202 red and near-infrared region. Our results provide an alternative approach to the metalation and the
 203 push-pull functionalization methodologies to extended and to improve the chiroptical responses of
 204 the helicene molecules by taking advantages of the strong synergy between the chiral environment
 205 controlled by the helicene center and the interesting photophysical properties offered by the
 206 corresponding dye. The polymers based on the helicene unit that we presented in this work can be
 207 used as a new class of candidates for efficient CPL materials in optoelectronics and bioimaging
 208 applications.

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217

218 **References**

- 219 Anger, E.; Srebro, M.; Vanthuyne, N.; Toupet, L.; Rigaut, S.; Roussel, C.; Autschbach, J.; Crassous, J.; Réau, R.
220 Ruthenium-Vinylhelicenes: Remote Metal-Based Enhancement and Redox Switching of the
221 Chiroptical Properties of a Helicene Core. *J. Am. Chem. Soc.* **2012**, *134*, 15628-15631, doi:
222 10.1021/ja304424t.
- 223 Berova, N.; Nakanishi, K.; Woody, R. W, *Circular dichroism: principles and applications*; John Wiley & Sons,
224 2000.
- 225 Berova, N.; Polavarapu, P. L.; Nakanishi, K.; Woody, R. W, *Comprehensive chiroptical spectroscopy:*
226 *applications in stereochemical analysis of synthetic compounds, natural products, and biomolecules*;
227 John Wiley & Sons, 2012.
- 228 Biet, T.; Cauchy, T.; Sun, Q.; Ding, J.; Hauser, A.; Oulevey, P.; Burgi, T.; Jacquemin, D.; Vanthuyne, N.;
229 Crassous, J.; Avarvari, N. Triplet state CPL active helicene-dithiolene platinum bipyridine complexes.
230 *Chem Commun (Camb)* **2017**, *53*, 9210-9213, doi: 10.1039/c7cc05198k.
- 231 Brandt, J. R.; Wang, X.; Yang, Y.; Campbell, A. J.; Fuchter, M. J. Circularly Polarized Phosphorescent
232 Electroluminescence with a High Dissymmetry Factor from PHOLEDs Based on a Platinahelicene. *J.*
233 *Am. Chem. Soc.* **2016**, *138*, 9743-9746, doi: 10.1021/jacs.6b02463.
- 234 Bouvier, R.; Durand, R.; Favereau, L.; Srebro-Hooper, M.; Dorcet, V.; Roisnel, T.; Vanthuyne, N.; Vesga, Y.;
235 Donnelly, J.; Hernandez, F.; Autschbach, J.; Trolez, Y.; Crassous, J. Helicenes Grafted with
236 1,1,4,4-Tetracyanobutadiene Moieties: π -Helical Push-Pull Systems with Strong Electronic Circular
237 Dichroism and Two-Photon Absorption. *Chem. Eur. J* **2018**, *24*, 14484-14494, doi:
238 10.1002/chem.201802763.
- 239 Carr, R.; Evans, N. H.; Parker, D. Lanthanide complexes as chiral probes exploiting circularly polarized
240 luminescence. *Chem. Soc. Rev.* **2012**, *41*, 7673-7686, doi: 10.1039/C2CS35242G.
- 241 Chen, C.-F.; Shen, Y. *Helicene Chemistry: From Synthesis to Applications*; Springer, 2016.
- 242 Data, P.; Kurowska, A.; Pluczyk, S.; Zassowski, P.; Pander, P.; Jedrysiak, R.; Czwartosz, M.; Otulakowski, L.;
243 Suwinski, J.; Lapkowski, M.; Monkman, A. P. Exciplex Enhancement as a Tool to Increase OLED Device
244 Efficiency. *The Journal of Physical Chemistry C* **2016**, *120*, 2070-2078, doi: 10.1021/acs.jpcc.5b11263.
- 245 Dhbaibi, K.; Favereau, L.; Srebro-Hooper, M.; Jean, M.; Vanthuyne, N.; Zinna, F.; Jamoussi, B.; Di Bari, L.;
246 Autschbach, J.; Crassous, J. Exciton coupling in diketopyrrolopyrrole-helicene derivatives leads to red
247 and near-infrared circularly polarized luminescence. *Chem. Sci.* **2018**, *9*, 735-742, doi:
248 10.1039/C7SC04312K.
- 249 Dhbaibi, K.; Favereau, L.; Crassous, J. Enantioenriched Helicenes and Helicenoids Containing Main-Group
250 Elements (B, Si, N, P). *Chem. Rev.* **2019**, *119*, 8846-8953, doi: 10.1021/acs.chemrev.9b00033.
- 251 Dhbaibi, K.; Favereau, L.; Srebro-Hooper, M.; Quinton, C.; Vanthuyne, N.; Arrico, L.; Roisnel, T.; Jamoussi, B.;
252 Poriel, C.; Cabanetos, C.; Autschbach, J.; Crassous, J. Modulation of circularly polarized luminescence
253 through excited-state symmetry breaking and interbranched exciton coupling in helical push-pull
254 organic systems. *Chem. Sci.* **2020**, doi: 10.1039/C9SC05231C.
- 255 Gingras, M. One hundred years of helicene chemistry. Part 3: applications and properties of carbohelicenes.
256 *Chem. Soc. Rev.* **2013**, *42*, 1051-1095, doi: 10.1039/C2CS35134J.
- 257 Grzybowski, M.; Gryko, D. T. Diketopyrrolopyrroles: Synthesis, Reactivity, and Optical Properties. *Adv. Opt.*
258 *Mater* **2015**, *3*, 280-320, doi:10.1002/adom.201400559.
- 259 Han, J.; Guo, S.; Lu, H.; Liu, S.; Zhao, Q.; Huang, W. Recent Progress on Circularly Polarized Luminescent
260 Materials for Organic Optoelectronic Devices. *Adv. Opt. Mater* **2018**, *6*, 1800538,
261 doi:10.1002/adom.201800538.

262 Heyer, E.; Lory, P.; Leprince, J.; Moreau, M.; Romieu, A.; Guardigli, M.; Roda, A.; Ziessel, R. Highly Fluorescent
263 and Water-Soluble Diketopyrrolopyrrole Dyes for Bioconjugation. *Angew. Chem. Int. Ed.* **2015**, *54*,
264 2995-2999, doi: 10.1002/anie.201411274.

265 Longhi, G.; Castiglioni, E.; Koshoubu, J.; Mazzeo, G.; Abbate, S. Circularly Polarized Luminescence: A Review
266 of Experimental and Theoretical Aspects. *Chirality* **2016**, *28*, 696-707, doi: 10.1002/chir.22647.

267 Tanaka, H.; Inoue, Y.; Mori, T. Circularly Polarized Luminescence and Circular Dichroisms in Small Organic
268 Molecules: Correlation between Excitation and Emission Dissymmetry Factors. *ChemPhotoChem*
269 **2018**, *2*, 386-402, doi:10.1002/cptc.201800015.

270 Huo, L.; Hou, J.; Chen, H.-Y.; Zhang, S.; Jiang, Y.; Chen, T. L.; Yang, Y. Bandgap and Molecular Level Control of
271 the Low-Bandgap Polymers Based on 3,6-Dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione
272 toward Highly Efficient Polymer Solar Cells. *Macromolecules* **2009**, *42*, 6564-6571, doi:
273 10.1021/ma9012972.

274 Kaur, M.; Choi, D. H. Diketopyrrolopyrrole: brilliant red pigment dye-based fluorescent probes and their
275 applications. *Chem. Soc. Rev.* **2015**, *44*, 58-77, doi: 10.1039/C4CS00248B.

276 Kumar, J.; Nakashima, T.; Tsumatori, H.; Mori, M.; Naito, M.; Kawai, T. Circularly Polarized Luminescence in
277 Supramolecular Assemblies of Chiral Bichromophoric Perylene Bisimides. *Chem. Eur. J* **2013**, *19*,
278 14090-14097, doi: 10.1002/chem.201302146.

279 Kumar, J.; Nakashima, T.; Kawai, T. Inversion of Supramolecular Chirality in Bichromophoric Perylene
280 Bisimides: Influence of Temperature and Ultrasound. *Langmuir* **2014**, *30*, 6030-6037, doi:
281 10.1021/la500497g.

282 Kumar, J.; Nakashima, T.; Kawai, T. Circularly Polarized Luminescence in Chiral Molecules and Supramolecular
283 Assemblies. *J. Phys. Chem. Lett* **2015**, *6*, 3445-3452, doi: 10.1021/acs.jpcclett.5b01452.

284 Kumar, J.; Tsumatori, H.; Yuasa, J.; Kawai, T.; Nakashima, T. Self-Discriminating Termination of Chiral
285 Supramolecular Polymerization: Tuning the Length of Nanofibers. *Angew. Chem. Int. Ed.* **2015**, *54*,
286 5943-5947, doi: 10.1002/anie.201500292.

287 Langhals, H.; Hofer, A.; Bernhard, S.; Siegel, J. S.; Mayer, P. Axially Chiral Bichromophoric Fluorescent Dyes. *J.*
288 *Org. Chem.* **2011**, *76*, 990-992, doi: 10.1021/jo102254a.

289 Longhi, G.; Castiglioni, E.; Koshoubu, J.; Mazzeo, G.; Abbate, S. Circularly Polarized Luminescence: A Review
290 of Experimental and Theoretical Aspects. *Chirality* **2016**, *28*, 696-707, doi: 10.1002/chir.22647.

291 Maeda, H.; Bando, Y. Recent progress in research on stimuli-responsive circularly polarized luminescence
292 based on π -conjugated molecules. *Pure Appl. Chem.* **2013**, *85*, 1967-1978, doi: 10.1351/pac-con-12-
293 11-09.

294 Meng, L.; Wei-Bin, L.; Lei, F.; Chuan-Feng, C. Recent Progress on Circularly Polarized Luminescence of Chiral
295 Organic Small Molecules. *Acta Chim. Sin.* **2017**, *75*, 1150-1163, doi: 10.6023/A17090440

296 Nielsen, C. B.; Turbiez, M.; McCulloch, I. Recent Advances in the Development of Semiconducting
297 DPP-Containing Polymers for Transistor Applications. *Adv. Mater.* **2013**, *25*, 1859-1880,
298 doi:10.1002/adma.201201795.

299 Nishimura, H.; Tanaka, K.; Morisaki, Y.; Chujo, Y.; Wakamiya, A.; Murata, Y. Oxygen-Bridged
300 Diphenylnaphthylamine as a Scaffold for Full-Color Circularly Polarized Luminescent Materials. *J. Org.*
301 *Chem.* **2017**, *82*, 5242-5249, doi: 10.1021/acs.joc.7b00511.

302 Palai, A. K.; Mishra, S. P.; Kumar, A.; Srivastava, R.; Kamalasanan, M. N.; Patri, M. Synthesis and
303 Characterization of Red-Emitting Poly(aryleneethynylene)s Based on
304 2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP). *Macromol.*
305 *Chem. Phys.* **2010**, *211*, 1043-1053, doi: 10.1002/macp.200900706.

306 Pascal, S.; Besnard, C.; Zinna, F.; Di Bari, L.; Le Guennic, B.; Jacquemin, D.; Lacour, J. Zwitterionic [4]helicene:
307 a water-soluble and reversible pH-triggered ECD/CPL chiroptical switch in the UV and red spectral
308 regions. *Org. Biomol. Chem* **2016**, *14*, 4590-4594, doi: 10.1039/C6OB00752J.

309 Riehl, J. P.; Richardson, F. S. Circularly polarized luminescence spectroscopy. *Chem. Rev.* **1986**, *86*, 1-16, doi:
310 10.1021/cr00071a001.

311 Saleh, N.; Srebro, M.; Reynaldo, T.; Vanthuyne, N.; Toupet, L.; Chang, V. Y.; Muller, G.; Williams, J. A. G.;
312 Roussel, C.; Autschbach, J.; Crassous, J. enantio-Enriched CPL-active helicene–bipyridine–rhenium
313 complexes. *Chem. Commun.* **2015**, *51*, 3754-3757, doi: 10.1039/C5CC00453E.
314 Sánchez-Carnerero, E. M.; Moreno, F.; Maroto, B. L.; Agarrabeitia, A. R.; Ortiz, M. J.; Vo, B. G.; Muller, G.;
315 Moya, S. d. I. Circularly Polarized Luminescence by Visible-Light Absorption in a Chiral O-BODIPY Dye:
316 Unprecedented Design of CPL Organic Molecules from Achiral Chromophores. *J. Am. Chem. Soc.*
317 **2014**, *136*, 3346-3349, doi: 10.1021/ja412294s.
318 Sakai, H.; Kubota, T.; Yuasa, J.; Araki, Y.; Sakanoue, T.; Takenobu, T.; Wada, T.; Kawai, T.; Hasobe, T.
319 Protonation-induced red-coloured circularly polarized luminescence of [5]carbohelicene fused by
320 benzimidazole. *Org. Biomol. Chem* **2016**, *14*, 6738-6743, doi: 10.1039/C6OB00937A.
321 Shen, C.; Anger, E.; Srebro, M.; Vanthuyne, N.; Deol, K. K.; Jefferson, T. D.; Muller, G.; Williams, J. A. G.;
322 Toupet, L.; Roussel, C.; Autschbach, J.; Réau, R.; Crassous, J. Straightforward access to mono- and bis-
323 cycloplatinated helicenes displaying circularly polarized phosphorescence by using crystallization
324 resolution methods. *Chem. Sci.* **2014**, *5*, 1915-1927, doi: 10.1039/C3SC53442A.
325 Shen, C.; Gan, F.; Zhang, G.; Ding, Y.; Wang, J.; Wang, R.; Crassous, J.; Qiu, H. Tunable Circularly Polarized
326 Luminescence of Helicene-Derived Aggregation-Induced Emission Adducts, *Materials Chemistry*
327 *Frontiers* **2020**, doi:10.1039/C9QM00652D.
328 Sheng, Y.; Ma, J.; Liu, S.; Wang, Y.; Zhu, C.; Cheng, Y. Strong and Reversible Circularly Polarized Luminescence
329 Emission of a Chiral 1,8-Naphthalimide Fluorophore Induced by Excimer Emission and Orderly
330 Aggregation. *Chem. Eur. J* **2016**, *22*, 9519-9522, doi: 10.1002/chem.201600891.
331 Tsumatori, H.; Nakashima, T.; Kawai, T. Observation of Chiral Aggregate Growth of Perylene Derivative in
332 Opaque Solution by Circularly Polarized Luminescence. *Org. Lett.* **2010**, *12*, 2362-2365, doi:
333 10.1021/ol100701w.
334 Wu, X. F.; Fu, W. F.; Xu, Z.; Shi, M.; Liu, F.; Chen, H. Z.; Wan, J. H.; Russell, T. P. Spiro Linkage as an Alternative
335 Strategy for Promising Nonfullerene Acceptors in Organic Solar Cells. *Adv. Funct. Mater.* **2015**, *25*,
336 5954-5966, doi: 10.1002/adfm.201502413.
337 Zhao, W.-L.; Li, M.; Lu, H.-Y.; Chen, C.-F. Advances in helicene derivatives with circularly polarized
338 luminescence. *Chem. Commun.* **2019**, *55*, 13793-13803, doi: 10.1039/C9CC06861A.
339 Zinna, F.; Di Bari, L. Lanthanide Circularly Polarized Luminescence: Bases and Applications. *Chirality* **2015**, *27*,
340 1-13, doi:10.1002/chir.22382.
341 de Bettencourt-Dias, A. *Luminescence of lanthanide ions in coordination compounds and nanomaterials*; John
342 Wiley & Sons, 2014.
343 Zinna, F.; Giovanella, U.; Bari, L. D. Highly Circularly Polarized Electroluminescence from a Chiral Europium
344 Complex. *Adv. Mater.* **2015**, *27*, 1791-1795, doi: 10.1002/adma.201404891.
345 Zinna, F.; Pasini, M.; Galeotti, F.; Botta, C.; Di Bari, L.; Giovanella, U. Design of Lanthanide-Based OLEDs with
346 Remarkable Circularly Polarized Electroluminescence. *Adv. Funct. Mater.* **2017**, *27*, 1603719, doi:
347 10.1002/adfm.201603719.
348 Zinna, F.; Di Bari, L. In *Lanthanide-Based Multifunctional Materials*; Martín-Ramos, P.; Ramos Silva, M., Eds.;
349 Elsevier, 2018.

351 **2 Author Contributions**

352 Kais Dhbaibi and Chengshuo Shen synthesized and characterized the molecules; Marion Jean and
353 Nicolas Vanthuyne performed the HPLC resolution; Thierry Roisnel performed the X-ray analysis;
354 Marcin Górecki performed CPL measurements; Bassem Jamoussi, Ludovic Favereau and Jeanne
355 Crassous supervised the work, analyzed the results and wrote the manuscript.

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